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(71) Applicant(s)

Reckitt & Colman Inc

(Incorporated in USA - Delaware)

225 Summit Avenue, MONTVALE, New Jersey 07645,  
United States of America

(72) Inventor(s)

James Chi-Cheng Feng

(74) Agent and/or Address for Service

Nigel P Sanderson

Reckitt & Colman plc, Group Patents Department,  
Dansom Lane, HULL, HU8 7DS, United Kingdom

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(54) Alkaline aqueous hard surface cleaning compositions

(57) Alkaline aqueous hard surface cleaning compositions which exhibit good cleaning efficacy against hardened dried or baked on greasy soil deposits which are storage stable, and are not undesirably irritating to the skin or mucous tissues of the user, comprise in percent by weight (based on 100% total weight of a composition):

0.01 - 0.85%wt. nonionic surfactant compound based on an amine oxide;

0 - 1.5%wt. chelating agent;

0.01 - 2.5%wt. caustic;

3.0 - 9.0%wt. glycol ether solvent system comprising one glycol ether or glycol ether acetate solvent having a solubility in water of not more than 20%wt., and a second glycol ether or glycol ether acetate having a solubility of approximately 100%wt., wherein the ratio of the former to the latter is from 0.5:1 to 1.5:1;

0 - 5.0%wt. of a water soluble amine containing organic compound;

0 - 2.5%wt. soil anti-redeposition agent;

0 - 2.5%wt. optional constituents.

The compositions contain no anionic or cationic type surfactant constituents, and include no more than 10%wt. of volatile organic constituents (VOCs).

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## ALKALINE AQUEOUS HARD SURFACE CLEANING COMPOSITIONS

5       The present invention relates to hard surface cleaners which are particularly useful in the cleaning of greasy soil laden surfaces. More particularly the present invention relates to hard surface cleaning compositions which are particularly useful in the cleaning of hardened or baked-on greasy soils on hard surfaces.

10       A wide variety of cleaning compositions which are effective in the cleaning of hard surfaces, such as surfaces normally encountered in kitchens and bathrooms, are known to the art. Many such compositions provide specifically directed cleaning benefits which are targeted at specific types of stains and soils deposited on said hard surfaces. These include, for example, mineral and salt deposits which are known also as hard water stains. Further types of stain which are particularly difficult to remove are aged, dried or baked on stains which are  
15 frequently the residues of cooking oils and greases. Such materials are typically not difficult to remove where such deposits are light and/or the material has not yet been permitted sufficient time to dry and harden. However, the converse is also true; after being baked on or dried, such residues of cooking oils and greases are extremely difficult to remove with most cleaning compositions.

20       A commercially acceptable cleaning composition, in order to be considered particularly useful to a consumer must demonstrate excellent efficacy in the removal of such dried or baked on greasy stains and soils.

25       A further characteristic which such a commercially acceptable cleaning composition must possess is long term stability. Particularly, a commercially acceptable cleaning composition must exhibit an appreciable shelf stability following its formulation so that it continues to exhibit excellent cleaning efficacy against dried or baked on greasy stains and soils even after several months of shelf life.

30       A still further characteristic of a commercially acceptable cleaning composition is a sufficiently low level of dermal and/or ocular irritation, such that no unacceptable hazard is associated with the use of such a composition by a consumer.

      From the foregoing, then it is apparent that there is a real and continuing need in the art to produce improved cleaning compositions which are especially useful in the removal of dried or baked on greasy stains and soils, and which satisfy further characteristics required for such a product in order to be considered commercially acceptable.

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Such a need is satisfied by the present inventive compositions which are aqueous hard surface cleaning compositions particularly beneficial in the removal of greasy stains and soils on hard surfaces, especially where such stains and soils are hardened or baked on.

Accordingly, one aspect the present invention provides a shelf stable, aqueous hard surface cleaning composition which is particularly effective against aged  
5 or baked on greasy stains and soils, which composition comprises in percent by weight (based on 100% total weight of a composition):

- 0.01 - 0.85% nonionic surfactant compound based on an amine oxide;
- 0 - 1.5% chelating agent;
- 10 0.01 - 2.5% caustic;
- 3.0 - 9.0% glycol ether solvent system comprising one glycol ether or glycol ether acetate solvent having a solubility in water of not more than 20%wt., and a second glycol ether or glycol ether acetate having a solubility of approximately 100%wt., wherein the ratio of the former to the latter is from 0.5:1 to 1.5:1;
- 15 0 - 5.0% of a water soluble amine containing organic compound;
- 0 - 2.5% soil anti-redeposition agent;
- 0 - 2.5% optional constituents
- to 100% water.

The compositions according to the invention are further characterized in that they contain no  
20 further anionic or cationic type surfactant constituents. The compositions of the invention also include no more than 10%wt. of volatile organic constituents (VOCs) of which greater amounts are undesirable from an environmental standpoint.

According to one preferred embodiment of the invention, there is provided a shelf stable, aqueous hard surface cleaning composition having a pH of at least 12.5 which is  
25 particularly effective against aged or baked on greasy stains and soils and comprises in percent by weight (based on 100% total weight of a composition):

- 0.5 - 0.8%wt. of the amine oxide based nonionic surfactant compound;
- 0.2 - 0.6%wt. salt of ethylenediamine tetraacetic acid;
- 0.1 - 0.5%wt. alkali metal hydroxide;
- 30 1.5 - 4.0%wt. alkanolamine;
- 5.0 - 7.0%wt. of a glycol ether solvent system comprising one glycol ether solvent having a solubility in water of not more than 20%wt., and a second glycol ether having a solubility of about 100%wt. in water, wherein the ratio of the former to the latter is from 0.5:1 to 1.5:1;

0 - 5.0%wt. of the water soluble amine containing organic compound;  
0 - 0.7%wt. of the soil anti-redeposition agent;  
0 - 1.0%wt. optional constituents  
to 100%wt. water.

5 Desirably, the amine oxide nonionic surfactant compound is lauryl dimethyl amine oxide, the first glycol ether solvent is propylene glycol n-butyl ether, and the second glycol ether solvent is dipropylene glycol methyl ether.

According to another preferred embodiment of the invention, there is provided a shelf stable, aqueous hard surface cleaning composition having a pH of at least 12.5 which is particularly effective against aged or baked on greasy stains and soils and comprises in percent  
10 by weight (based on 100% total weight of a composition):

0.5 - 0.8%wt. of the amine oxide based nonionic surfactant compound;

0.1 - 1.5%wt. of a chelating agent, preferably selected from citrates, gluconates and glucoheptonates, particularly sodium salts thereof;

15 0.1 - 0.5%wt. alkali metal hydroxide;

1.5 - 4.0%wt. alkanolamine;

5.0 - 7.0%wt. of a glycol ether solvent system comprising one glycol ether solvent having a solubility in water of not more than 20%wt., and a second glycol ether having a solubility of about 100%wt. in water, wherein the ratio of the former to the  
20 latter is from 0.5:1 to 1.5:1;

0 - 5.0%wt. of the water soluble amine containing organic compound;

0 - 0.7%wt. of the soil anti-redeposition agent;

0 - 1.0%wt. optional constituents

to 100%wt. water.

25 Desirably, the amine oxide nonionic surfactant compound is lauryl dimethyl amine oxide, the first glycol ether solvent is propylene glycol n-butyl ether, and the second glycol ether solvent is dipropylene glycol methyl ether. An advantage of this embodiment of the invention is the elimination of ethylenediaminetetraacetic acid from the formulation which may be desirable from an environmental perspective.

30 According to a further aspect of the invention there is provided a method for cleaning a hard surface having baked-on greasy or oily stains which comprises the step of: applying an effective amount of the composition noted above for the removal of the said stains.

The compositions according to the invention may be further characterized in that they are effective for the removal of common types of stains and soil deposits frequently

encountered on hard surfaces in food preparation environments, and are particularly effective in the removal of aged, dried, hardened or baked-on stains based on residues of cooking oils and greases. The compositions of the invention desirably exhibit good shelf stability, particularly as demonstrated by accelerated shelf life testing wherein the compositions are  
5 stored in temperature to 120°F (48.8°C) for a one week period. The compositions of the invention are also not undesirably irritating to the skin.

The compositions according to the invention include at least one nonionic surfactant compound based on an amine oxide. One general class of useful amine oxides include alkyl di (lower alkyl) amine oxides in which the first alkyl group has about 10-20, and preferably  
10 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. The lower alkyl groups include between 1 and 7 carbon atoms. Examples include lauryl dimethyl amine oxide, myristyl dimethyl amine oxide, and those amine oxides in which the alkyl group is a mixture of different amine oxides, e.g., dimethyl cocoamine oxide, dimethyl (hydrogenated tallow) amine oxide, and myristyl/palmityl dimethyl amine oxide.

15 A further class of useful amine oxides include alkyl di(hydroxy lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallowamine oxide; and bis(2hydroxyethyl) stearylamine oxide.

20 Further useful amine oxides include those which may be characterized as alkylamidopropyl di(lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide; and

25 Additional useful amine oxides include alkylmorpholine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated.

Particularly useful are those amine oxides which are presently commercially available under the trademark AMMONYX (commercially available from the Stepan Co., Northfield,  
30 IL) i.e., AMMONYX CDO (cocoamido propyl dimethyl amine oxide); AMMONYX CO (cetyl dimethyl amine oxide); AMMONYX DMCD-40 (lauryl dimethyl amine oxide); AMMONYX LO (lauryl dimethyl amine oxide); AMMONYX MCO (myristyl cetyl dimethyl amine oxide); AMMONYX MO (myristyl dimethyl amine oxide).

The amine oxide surfactant compound may be present in an amount of from 0.01 to  
35 0.85 %wt. based on the total weight of the composition, but more desirably from 0.1 to 0.75%.

The compositions of the invention include a chelating agent which is effective in complexing with the metal ions commonly found in fats, oils and other organic soils, especially in greasy stains and soils. Examples of chelating agents which can be employed include gluconic acid, tartartic acid, citric acid, oxalic acid, lactic acid,

5 ethylenediaminetetraacetic acid, N-hydroxyethylethylenediamine triacetic acid, nitrilotriacetic acid, diethylene triamine pentaacetic acid, and their water soluble salts, especially the alkali metal salts and particularly the sodium salts. Particularly advantageously used are di-, tri- and tetrasodium salts of ethylenediaminetetraacetic acid, especially tetrasodium salts thereof.

However, it is to be understood that where such di-, tri- and tetra-sodium salts of

10 ethylenediaminetetraacetic acid pose a concern from an environmental viewpoint, they may be eliminated from the formulations, and/or one or more further chelating agents which are more acceptable may be used in the formulations; such acceptable chelating agents include citrate, gluconate or glucoheptonate salts, particularly sodium citrate, sodium gluconate and sodium glucoheptonate.

15 The chelating agents may be desirably included in any effective amounts, with amounts of from 0 - 1.5%wt.. being a particularly useful weight range. In certain areas, the use of chelating agents may be undesired, in which case it may be omitted from the inventive compositions. According to certain preferred embodiments where chelating agents are present, they are used in an amount to comprise from 0.01 to 1.0%wt.. based on the total  
20 weight of the cleaning composition of which they form a part.

The compositions of the invention also include a caustic which is desirably present in sufficient amounts to ensure that the overall pH of the compositions is at least 11.5 or greater, especially at least 13 or greater, and further, to provide an efficacious cleaning benefit against hardened, dried or baked on greasy soil deposits on hard surfaces.

25 Useful as the caustic constituent according to the invention are any one or more calcined or anhydrous alkali metal carbonates, preferably a sodium or potassium carbonate, especially sodium carbonate. Also useful are corresponding phosphates especially trisodium phosphates, sodium tripolyphosphate and disodium hydrogen phosphate. Bicarbonates, silicates and borates may also be used, preferably as sodium salts, e.g., borax, sodium  
30 bicarbonate and sodium silicates such as  $\text{Na}_2\text{O}:\text{SiO}_2$ . Also useful and preferred for use as the caustic constituent are one or more calcined or anhydrous alkali metal hydroxides, particularly sodium hydroxide. The caustic constituent may be supplied in any of a variety of forms including solid forms, as well as dispersions such as aqueous dispersions, mixtures or solutions of one or more caustic constituents in a volume of water.

The compositions of the invention desirably include one or more water soluble, amine-containing organic compounds which are effective as a protein denaturant. Particularly advantageously employed as this component are alkanolamides which may include single or multiple amine groups, of which mono- and di-(lower alkyl)amines such as monoethanolamine  
5 are most preferred.

The amine-containing organic compounds are desirably included in the inventive compositions so to comprise from 0.5 to 5.0%wt.. based on the total weight of the compositions, but even more desirably comprise from 1.5 - 4.0%wt. based on the total weight of the inventive compositions.

10 The hard surface cleaning compositions of the invention further include a glycol ether solvent system comprising one glycol ether solvent having a solubility in water of not more than 20%wt., and a second glycol ether having a solubility in water of approximately 100%wt., wherein the ratio of the former to the latter is from 0.5:1 to 1.2:1.

Useful solvents which may be incorporated in the inventive compositions include  
15 glycol ethers desirably having the general structure  $Ra-O-Rb-OH$ , as well as glycol ether acetates having the general structure  $Ra-O-Rb-COOCH_3$ , wherein  $Ra$  is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms, and  $Rb$  is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Preferred are glycol ethers and glycol acetates having one to five glycol monomer units.  
20 Particularly useful as the glycol ether or glycol ether acetate solvent having a solubility in water of not more than 20%wt. are, by way of example (and not by limitation): propylene glycol methyl ether acetate, dipropylene glycol methyl ether acetate, propylene glycol n-butyl ether acetate, dipropylene glycol n-butyl ether acetate, tripropylene glycol n-butyl ether acetate, propylene glycol phenyl ether acetate, and dipropylene glycol n-propyl ether acetate,  
25 of which propylene glycol n-butyl ether acetate is especially advantageously employed in the inventive compositions.

As noted, these solvents exhibit a solubility in water of not more than 20%wt., which is approximately equal to the millilitres of a the specific solvent per 100 ml of water and, for the purposes of this specification, are considered to be equivalent units of measure. More  
30 desirably however, these solvents having limited solubility in water are those which exhibit no more than 9%wt. in water, (or 9ml solvent/100 ml water) and even more desirably include those which exhibit from 1 to 7%wt. in water (or 1 to 7 ml solvent/100 ml water).

Particularly advantageously used as the glycol ether solvent are, by way of example (and not by limitation): propylene glycol methyl ether, dipropylene glycol methyl ether,  
35 tripropylene glycol methyl ether, propylene glycol n-propyl ether, ethylene glycol n-butyl

ether, diethylene glycol n-butyl ether, triethylene glycol butyl ether, diethylene glycol methyl ether, triethylene glycol methyl ether, ethylene glycol phenyl ether, as well as aromatic based glycol ethers.

As noted, these solvents exhibit a solubility in water of approximately 100%wt. in water and more, which is approximately equal to the millilitres of the specific solvent per 100 ml of water and for the purposes of this specification are considered to be equivalent units of measure. Desirably however, these solvents having high solubility in water are those which exhibit about 100%wt. in water, (or 100ml solvent/100 ml water) and even more desirably include those which are considered infinitely soluble in water.

Such solubility criteria which are discussed herein may be ascertained by routine empirical procedures; alternatively, data regarding the solubility characteristics of such glycol ethers and glycol ether acetates may be found from readily available published data. Examples of such empirical procedures as well as published solubility data may be found, for example, in Handbook of Solubility Parameters and Other Properties', A.F.M. Barton (CRC Press, Boca Raton, FL) as well as from technical reference sheets and publications available from suppliers of such materials.

These solvents are presently commercially available in the DOWANOL® glycol ether and glycol ether acetate series available from The Dow Chemical Company, (Midland MI).

The present inventor has discovered that the use of a single glycol ether or glycol ether acetate as an organic solvent may provide a formulation exhibiting good cleaning characteristics, but such formulations have also been found by the inventor to be phase unstable with degradation of such a formulation being observed when subjected to accelerated aging conditions, namely being heated to 120°F (49°C) for a period of time. Such a formulation is not particularly shelf stable, nor is necessarily suitable for commercial use. Surprisingly, the inventor has found that the use of two solvents, each based on a glycol ether or glycol ether acetate but of markedly different water solubility, provides good cleaning characteristics, and at the same time maintains good formulation stability when subjected to such accelerated aging conditions.

The inventor has also surprisingly discovered that the addition of a further anionic or cationic surfactant to the formulation causes an appreciable decrease in the cleaning properties of such a composition. Such would not be expected in the art, as the inclusion of such surfactants would normally be expected to facilitate the penetration and removal of oily stains and oily soil deposits.

Water forms a further constituent according to the invention, and is added to the constituents noted above in an amount to provide 100% by weight of the composition. The



water may be provided from a variety of sources, including tap water, but is preferably distilled and is most preferably deionized or 'soft' water. If the water is tap water, it is preferably substantially free of any undesirable impurities such as organics or inorganics, especially minerals salts which are present in hard water and may interfere with the operation of one or more of the essential constituents, as well as other optional constituents of the hard surface cleaning compositions according to the invention.

The compositions of the invention optionally, but desirably, include a soil anti-redeposition agent which may include any of those which are currently known and used in the art relating to hard surface cleaners. Such include by way of example, compositions based on polyacrylic acids and salts thereof, fatty amides complexes, silicone copolymers, polyvinylpyrrolidone, synthetic hectorite, colloidal silica, styrene maleic anhydride copolymers, as well as esters and partial esters thereof, polycarboxylate copolymers, as well as others not specifically elucidated here. When included in the inventive compositions, particularly useful agents are those based on polyacrylic acid as well as salts thereof. When included in the compositions, such soil anti-redeposition agents need be present in only minor amounts, with amount of up to 2.5%wt. generally found to be effective, but even more desirably lesser amounts are used such as up to about 0.7%wt. being typically sufficiently effective.

The compositions of the invention may also include one or more further optional constituents.

One advantageously utilized optional constituent is a water soluble or dispersible preservative, since a significant portion of the formulation comprises water. Such water soluble preservatives include compositions such as parabens including methyl parabens and ethyl parabens, glutaraldehyde, formaldehyde, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazoline-3-one, and mixtures thereof. One exemplary composition is a combination of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one where the amount of either component may be present in the mixture anywhere from 0.01 to 99.99 weight percent, based on the total amount of the preservative. Also useful is a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one marketed under the trademark KATHON CG/ICP as a preservative composition commercially available from Rohm and Haas (Philadelphia, PA). Further useful commercially available preservative compositions include for example: PROXEL GXL; GLYDANT®, a water soluble preservative based on DMDM hydantoin; GLYDANT Plus, a water soluble preservative based on DMDM hydantoin and iodopropyl butyl carbamate; and TEXTAMER 38 AD.

The hard surface cleaning compositions of the invention may also include one or more optional constituents including, but not limited to: buffers, pH buffering agents, fragrances, fragrance carriers and adjuvants which increase their miscibility in the aqueous compositions, colorants, hydrotropes, antifoaming agents, anti-oxidants, anti-corrosion agents particularly when formulated for use in a pressurized aerosol container, as well as others known to the art but not specifically mentioned herein. Such volatile materials, fragrances, fragrance carriers and adjuvants are not considered as VOCs in the compositions of the invention. One particularly desirable additive is a thickening agent, or other viscosity modifying agent such as those based on alginates and gums, e.g., xanthan gum.

It is to be noted that such optional constituents may be included in minor amounts, generally in total comprising no more than about 2.5%wt., of the total composition of which they form a part. It is to be further noted that particular care must be exercised in their inclusion and selection especially with respect to the total amount of VOCs which may be present in a composition, and also with regard to any detrimental effects to the overall cleaning and stability features of the compositions.

The benefits of the inventive compositions described in this specification include particularly: good removal of greasy soils and deposits on hard surfaces, particularly those which have been aged or "baked on", relatively low dermal irritation notwithstanding the alkaline nature of the compositions, exhibit shelf stability at room temperature (approx. 20°C) and preferred compositions exhibit good high temperature stability when heated to 120°F (49°C) for a period of 1 week, as well as ease in handling of the composition due to its readily pourable or pumpable characteristic. Further, when one or more of the optional constituents is added, i.e., fragrance, foaming agents, coloring agents, the aesthetic and consumer appeal of the product is improved.

Notwithstanding that the pH of preferred embodiments of compositions according to the present invention is in excess of 11, and desirably is about 13 and higher, it has been surprisingly been found that these formulations do not appear to be particularly irritating to the skin or mucous tissues of a consumer. Such is a surprising effect, as the alkaline character of the compositions and their correspondingly relatively high pH would be expected to be an irritant.

A hard surface cleaning composition according to the invention may be readily produced by adding one or more of the constituents to water, generally with the nonionic surfactant being added first, then adding the other components under stirring conditions at room temperature. Stirring continues until a homogenous mixture is produced, which is in a ready to use form.

Such a hard surface cleaning composition according to the invention is desirably provided as a ready to use product which may be directly applied to a hard surface. By way of example, hard surfaces suitable for cleaning with the composition include surfaces composed of refractory materials such as: glazed and unglazed tile, brick, porcelain, ceramics as well as  
5 stone including marble, granite, and other stones surfaces; glass; metals, especially stainless steel surfaces; plastics, e.g. polyester, vinyl; Fiberglass®, Formica®, Corian® and other hard surfaces known to the industry. Hard surfaces which are to be particularly denoted are kitchen fixtures and other surfaces associated with areas and equipment used in the preparation of foods such as stove and oven surfaces, other appliance surfaces, cabinets and countertop  
10 surfaces as well as walls and floor surfaces.

The hard surface cleaner composition provided according to the invention can be desirably provided as a ready to use product in a manually operated spray dispensing container. Such a typical container is generally made of synthetic polymer plastic material such as polyethylene, polypropylene, polyvinyl chloride or the like and includes spray nozzle, a dip  
15 tube and associated pump dispensing parts and is thus ideally suited for use in a consumer spray-and-wipe application. In such an application, the consumer generally applies an effective amount of the cleaning composition using the pump and within a few moments thereafter, wipes off the treated area with a cloth, towel such as a paper towel, or sponge. In certain applications, however, especially where undesirable stain deposits are heavy, the cleaning  
20 composition according to the invention may be left on the stained area until it has effectively loosened the stain deposits after which it may then be wiped off, rinsed off, or otherwise removed. For particularly heavy deposits of such undesired stains, multiple applications may also be used.

In a yet a further embodiment, the product according to the invention may be  
25 formulated so that it may be useful as an aerosol type product wherein it is discharged from a pressurized aerosol container. Known art propellants such as liquid propellants based on chlorofluorocarbons or propellants of the non-liquid form, i.e., pressurized gases, including carbon dioxide, air, nitrogen, as well as others, may be used, even though it is realized that chlorofluorocarbons are not generally used at this time due to environmental considerations. In  
30 such an application, the cleaning composition is dispensed by activating the release nozzle of said aerosol type container onto the stain and/or stain area and, in accordance with the manner as above-described a stain is treated and removed.

Whereas the present invention is intended to be used in the types of liquid forms described, nothing in this specification shall be understood as to limit the use of the  
35 composition according to the invention with a further amount of water to form a cleaning

solution therefrom. In such a proposed diluted cleaning solution, the greater the proportion of water added to form said cleaning dilution, the greater will be the reduction of the rate and/or efficacy of the thus formed cleaning solution. Accordingly, longer residence times upon the stain to effect their loosening and/or the usage of greater amounts may be necessitated.

- 5 Conversely, nothing in the specification shall be also understood to limit the forming of a super-concentrated cleaning composition based upon the composition described above. Such a super-concentrated ingredient composition is essentially the same as the cleaning compositions described above except in that it would include a lesser amount of water.

- 10 The hard surface cleaning compositions according to the invention are exemplified by the following exemplary formulations.

#### EXAMPLES

##### Preparation of Example Formulations:

- 15 Exemplary formulations illustrating certain preferred embodiments of the inventive compositions and described in more detail in Table 1 below were formulated in accordance with the following protocol.

- 20 Into a suitably sized vessel, a measured amount of water was provided after which the constituents were added in the following sequence: thickening agent, surfactants, solvents, acid and, lastly, the coloring and fragrance constituents. All of the constituents were supplied at room temperature, and mixing of the constituents was achieved by the use of a mechanical stirrer with a small diameter propeller at the end of its rotating shaft. Mixing, which generally lasted from 5 minutes to 120 minutes was maintained until the particular exemplary formulation appeared to be homogeneous. The exemplary compositions were readily pourable, and retained well mixed characteristics (i.e., stable mixtures) upon standing for extended periods, even in excess of 120 days. It is to be noted that the constituents may be added in any order, but it is preferred that water be the initial constituent provided to a mixing vessel or apparatus, as it is the major constituent and addition of the further constituents thereto is convenient.
- 25

The exact compositions of the example formulations are listed on Table 1, below, with the figures denoting weight percentages:

TABLE 1				
	Ex.1	Ex.2	Ex.3	Ex.4
amine oxide (30% actives)	2.0	2.0	2.0	2.0
EDTA salt (39% actives)	0.5	0.5	0.5	0.5
NaOH (50% actives)	0.8	0.8	0.8	0.8
monoethanolamine	3.0	3.0	3.0	3.0
glycol ether, low water soluble	3.0	2.8	2.8	3.0
glycol ether, high water soluble	3.7	3.7	3.7	3.7
soil anti-redeposition agent	---	0.5	0.5	0.5
fragrance	---	0.1	0.1	---
water	to 100	to 100	to 100	to 100

The identity of the individual constituents is more fully described on Table 2, below.

5

TABLE 2	
constituent:	description:
amine oxide (30% actives)	lauryl dimethyl amine oxide (30%wt. actives); nonionic surfactant, AMMONYX® LO (Stepan Co., Northfield IL)
EDTA salt	VERSENE® 100(39%wt. actives); tetrasodium salt of ethylenediaminetetraacetic acid
NaOH (50%)	caustic, (50%wt. actives) sodium hydroxide solution
monoethanolamine	2-aminoethanol (approx. 100%wt. actives)
glycol ether, low water soluble	propylene glycol n-butyl ether (approx. 100%wt. active) DOWANOL® PnB (Dow Chemical Co., Midland MI)
glycol ether, high water soluble	dipropylene glycol methyl ether (approx. 100%wt. active) DOWANOL® DPM (Dow Chemical Co., Midland MI)
soil anti-redeposition agent	proprietary composition, polyacrylic based; ACUSOL® 445N (Rohm and Haas Co., Philadelphia PA)
fragrance	commercially available proprietary composition

The compositions of Ex. 2 and Ex. 3 differed only in the use of different fragrance compositions.

For comparative evaluation against the formulations according to Examples 1 through 4 of Table 1, samples of a commercially available hard surface cleaning product advertised as particularly formulated for use on greasy stains was used. Such product was "FORMULA 409 All Purpose Cleaner" which was used as-is from its container, and is identified hereafter as "Comp."

### Cleaning Evaluation

Compositions according to the invention as embodied in the formulations of Table 1 described above, were evaluated against the comparative composition in order to determine their relative cleaning efficacies.

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#### Baked on Soil Test:

A test soil was prepared based on the following constituents: peanut oil 26.2% by weight; corn oil 14.5% by weight; cherry pie mix 14.5% by weight; 75% lean ground beef 14.5% by weight; ground pork 14.5% by weight; sodium glutamate 0.6% by weight; sodium chloride 0.6% by weight; and water 14.6% by weight. This test oil was prepared in 1,000 gram batches, after which it was placed in a ceramic baking dish and heated in an oven for two hours at 400°F (204.5°C). Afterwards, the oil portion, which is the test soil, was separated by decanting through several layers of fine cheesecloth from the remaining solids. The remaining filtrate, i.e., the test soil, was sufficiently filtered so as to be substantially clear and void of particle matter. The standard test soil was either used immediately or could be used subsequent to refrigeration if heated to approximately 100°F (38°C) and shaken to ensure homogenization thereof.

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The porcelain enamel test plates cut from an oven liner and having a light grayish color, were individually weighed. To each was applied 0.37 grams  $\pm$  0.05 grams of the test soil by brushing uniformly (which corresponds to 0.25 grams on a 4.5 inch by 4.5 inch (11.4 cm x 11.4 cm square plate). Subsequently each of the plates thus treated were reweighed to ensure the proper amount of soil deposited on each plate, after which these soiled plates were placed in aluminium baking trays. The tops of the trays were covered with aluminium foil, however, such covers did not contact the soil applied to each of the plates. These baking trays were placed in a large convection oven in a staggered position, and never at the bottom of the oven. The plates were baked for 45 minutes at 375°C (190.5°C) (which permitted the test soil to be "baked on"). Afterwards, the trays containing each of the treated plates were removed and allowed to cool. The test soil thus "baked on" onto each of the enamel plates was a light to medium brownish color and, when cooled, formed a slightly sticky film when touched.

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The cleaning efficacy of the formulations denoted were evaluated in accordance with the following general protocol, using the test plates prepared as described above.

First each of the plates were divided into two equal halves, using 1/2 inch (1.2 cm) wide masking tape thus separating a first side from a second side. The tape was positioned approximately centrally on each of the test plates, thereby approximately bisecting its surface prepared with the test stain.

Evaluations of the cleaning efficacy of the formulations according to the invention, as well as that of the comparative formulation, were formed in accordance with the following general manner.

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A 400 gram amount of a formulation according to Example 2 described in detail in Table 1 above was poured into a first plastic vessel. Similarly, a 400 gram sample of the comparative formulation was poured into a second vessel.

For each of the plates within the test, one of the bisected sides of the surface was inserted  
5 in the first container for a 10 minute period during which the formulation according to the invention was permitted to act upon the test soil. No agitation, physical scrubbing or wiping was performed during this soaking period. After this 10 minute soaking period, the plate was removed and rinsed under a flush of cold tap water. Afterwards, with a water dampened cellulose sponge, the sponge was lightly used to move any loosened soil from the surface of the plate.

10 The same protocol regarding the 10 minute soak time, the cold water wash and the light sponging was followed for the other side of the test plate, however, the comparative formulation was tested.

In the same manner, individual test plates were cleaned using the comparative composition and a formulation of Table 1.

15 Subsequently, the individual plates were then bordered on each of its remaining exterior edges with a ½ inch (1.2 cm) wide masking tape in preparation for a visual evaluation by a group of 20 panelists. The plates were laid out in a square matrix pattern and each of 20 panelists was asked to rate the plates by visual inspection. The panelists were asked to rate each plate individually, indicating their perception of soil removed, 0% being no soil removed to 100% indicating complete soil removal for each of the two halves of  
20 each test plate. These results indicate the relative efficacy of these formulations according to the invention, versus the comparative compositions.

Subsequently, based on these visual ranking results, the average of the differences between the rating reported by the panelists for each of the two cleaned sides of each test tile, which is reported in Table 3 below.

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TABLE 3	
Tile lab	76
Tile 2ab	71.45
Tile 3ab	85.75
Tile 4ab	84.6
Tile 5ab	77
Tile 6ab	68.35
Tile 7ab	61.8
Tile 8ab	55.2
Tile 9ab	52.4
Tile 10ab	65.65

These results were then evaluated in accordance with the standard statistical procedure, One Sample T-test at a 95% confidence interval which result indicated that the formulation according the

invention significantly outperformed the comparative composition, "FORMULA 409 All Purpose Cleaner" (The Clorox Company, Oakland, CA).

Wallboard Cleaning Test (ASTM D-4488)

Test soiled surfaces of painted Masonite wallboard were prepared generally in accordance with the test protocols outlined in ASTM D-4488(A2). In accordance with this test, a painted Masonite wallboard sample was soiled with a mixture of melted oily solids containing a small amount of carbon black, which is allowed to set overnight. Test cleaning compositions and/or comparative cleaning compositions were applied to a sponge which scrubs half of the wallboard sample utilizing a Gardner Washability Apparatus, a standard pressure and standard sponge stroke settings, in order to determine or quantify the cleaning efficiency of the formulations treated with an equal amount of each formulation and stroked an equal number of times. Equal amounts of the formulations were used "as is" and were not further diluted.

In determining the cleaning efficiency of each of the formulations, reflectance values were determined for each of the wallboard samples using a Minolta Chromameter which tested each wallboard at least three times. The mean reflectance values are reported below in Table 4 as well as in Table 5. In Table 4, the formulation according to Example 1 described on Table 1 was evaluated against the comparative composition. In Table 5, the formulation according to Example 4 described on Table 1 was evaluated against the comparative composition. Such reflectance values were then employed to calculate % Cleaning Efficiency according to the following formula:

$$\% \text{ Cleaning Efficiency} = \frac{R_c - R_s}{R_o - R_s} \times 100\%$$

wherein:

$R_c$  = % reflectance average after scrubbing solid tile;

$R_s$  = % reflectance average before cleaning soiled tile;

$R_o$  = % reflectance average original tile before soiling.



TABLE 4 Comparative Composition				
	Ro	Rs	Rc	% Cleaning Efficiency
Tile 1a	91.36	29.83	74.2	72.11117
Tile 2a	91.36	29.83	73.77	71.41232
Tile 3a	91.36	29.83	75.17	73.68763
Tile 4a	91.36	29.83	73.65	71.21729
Tile 5a	91.36	29.83	74.48	72.56623
Tile 6a	91.36	29.83	71.79	68.19438
Tile 7a	91.36	29.83	71.41	67.57679
Tile 8a	91.36	29.83	71.77	68.16187
Tile 9a	91.36	29.83	75.81	74.72778
Tile 10a	91.36	29.83	74.32	72.30619
Tile 11a	91.36	29.83	73.42	70.84349
Tile 12a	91.36	29.83	73.46	70.9085
Tile 13a	91.36	29.83	77.17	76.93808
Tile 14a	91.36	29.83	75.6	74.38648
Tile 15a	91.36	29.83	73.55	71.05477
Tile 16a	91.36	29.83	77.03	76.71055
Tile 17a	91.36	29.83	76.63	76.06046
Tile 18a	91.36	29.83	77.7	77.79945
Tile 19a	91.36	29.83	74.81	73.10255
Tile 20a	91.36	29.83	76.95	76.58053

TABLE 4 Example 1				
	Ro	Rs	Rc	% Cleaning Efficiency
Tile 1b	91.36	29.83	73.42	70.84349
Tile 2b	91.36	29.83	74.45	72.51747
Tile 3b	91.36	29.83	75.24	73.8014
Tile 4b	91.36	29.83	74.24	72.17617
Tile 5b	91.36	29.83	75.38	74.02893
Tile 6b	91.36	29.83	75.05	73.49261
Tile 7b	91.36	29.83	73.09	70.30717
Tile 8b	91.36	29.83	74.01	71.80237
Tile 9b	91.36	29.83	76.62	76.04421
Tile 10b	91.36	29.83	74.35	72.35495
Tile 11b	91.36	29.83	73.38	70.7848
Tile 12b	31.36	29.83	74.74	72.98879
Tile 13b	91.36	29.83	78.4	78.9371
Tile 14b	31.36	29.83	76.74	76.23923
Tile 15b	91.36	29.83	76.59	75.99545
Tile 16b	91.36	29.83	78.11	78.46579
Tile 17b	91.36	29.83	78.85	79.66845
Tile 18b	91.36	29.83	77.5	77.4744
Tile 19b	91.36	29.83	74.09	71.93239
Tile 20b	91.36	29.83	77.07	76.77556

These results were then statistically evaluated according to the Two Sample T-Test at a 95% confidence interval, which confirmed that at this high confidence level than the formulation of Ex. 1 according to the invention provided excellent cleaning results.

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TABLE 5 Comparative Composition				
	Ro	Rs	Rc	% Cleaning Efficiency
Tile 1a	93.64	28.42	78.46	76.72493
Tile 2a	93.64	28.42	81.6	81.53941
Tile 3a	93.64	28.42	79.54	78.38086
Tile 4a	93.64	28.42	77.44	75.16099
Tile 5a	93.64	28.42	80.34	79.60748
Tile 6a	93.64	28.42	79.48	78.28887
Tile 7a	93.64	28.42	80.67	80.11346
Tile 8a	93.64	28.42	80.28	79.51549
Tile 9a	93.64	28.42	80.1	79.2395
Tile 10a	93.64	28.42	79.81	78.79485
Tile 11a	93.64	28.42	82.66	83.16467
Tile 12a	93.64	28.42	80.98	80.58878
Tile 13a	93.64	28.42	77.18	74.76234
Tile 14a	93.64	28.42	78.72	77.12358
Tile 15a	93.64	28.42	80.52	79.88347
Tile 16a	93.64	28.42	80.7	80.15946
Tile 17a	93.64	28.42	79.92	78.96351
Tile 18a	93.64	28.42	78.91	77.4149
Tile 19a	93.64	28.42	79.94	78.99417
Tile 20a	93.64	28.42	81.69	81.6774
Tile 21a	93.64	28.42	80.89	80.45078
Tile 22a	93.64	28.42	80.85	80.38945
Tile 23a	93.64	28.42	80.09	79.22416
Tile 24a	93.64	28.42	83.02	83.71665
Tile 25a	93.64	28.42	79.78	78.74885
Tile 26a	93.64	28.42	80.11	79.25483
Tile 27a	93.64	28.42	82.9	83.53266
Tile 28a	93.64	28.42	83.11	83.85465
Tile 29a	93.64	28.42	82.4	82.76602

TABLE 5 Example 4				
	Ro	Rs	Rc	% Cleaning Efficacy
Title 1b	93.64	28.42	80.04	79.1475
Title 2b	93.64	28.42	81.25	81.00276
Title 3b	93.64	28.42	81.39	81.21742
Title 4b	93.64	28.42	82.61	83.08801
Title 5b	93.64	28.42	82.24	82.5207
Title 6b	93.64	28.42	82.25	82.53603
Title 7b	93.64	28.42	82.47	82.87335
Title 8b	93.64	28.42	83.76	84.85127
Title 9b	93.64	28.42	81.96	82.09138
Title 10b	93.64	28.42	83.42	84.32996
Title 11b	93.64	28.42	82.27	82.5667
Title 12b	93.64	28.42	83.69	84.74394
Title 13b	93.64	28.42	81.91	82.01472
Title 14b	93.64	28.42	81.72	81.7234
Title 15b	93.64	28.42	84.12	85.40325
Title 16b	93.64	28.42	83.06	83.77798
Title 17b	93.64	28.42	80.03	79.13217
Title 18b	93.64	28.42	81.99	82.13738
Title 19b	93.64	28.42	81.42	81.26342
Title 20b	93.64	28.42	82.62	83.10334
Title 21b	93.64	28.42	81.94	82.06072
Title 22b	93.64	28.42	82.88	83.50199
Title 23b	93.64	28.42	83.37	84.2533
Title 24b	93.64	28.42	83.02	83.71665
Title 25b	93.64	28.42	83.02	83.71665
Title 26b	93.64	28.42	83.16	83.93131
Title 27b	93.64	28.42	81.56	81.47807
Title 28b	93.64	28.42	83.78	84.88194
Title 29b	93.64	28.42	83.07	83.79331

These results were then statistically evaluated according to the Two Sample T-Test at a 95% confidence interval, which confirmed that at this high confidence level than the formulation of Ex. 4 according to the invention provided superior cleaning results as compared to the comparative composition.

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Claims:

1. An aqueous hard surface cleaning composition comprising (based on 100% total weight of said composition):
  - 0.01 - 0.85%wt. nonionic surfactant compound based on an amine oxide;
  - 0 - 1.5%wt. chelating agent;
  - 0.01% - 2.5%wt. caustic;
  - 3.0 - 9.0%wt. a glycol ether solvent system comprising one glycol ether or glycol ether acetate solvent having a solubility in water of not more than 20%wt., and a second glycol ether or glycol ether acetate having a solubility of about 100%wt. in water, wherein the ratio of the former to the latter is from 0.5:1 to 1.5:1
  - 0 - 5%wt. water soluble, amine containing organic compound; and
  - 0 - 2.5%wt. soil anti-redeposition agent.
2. A composition according to claim 1 wherein the nonionic surfactant compound is selected from an alkyl di(lower alkyl) amine oxide compound containing 10-20 carbon atoms in its first alkyl group, an alkyl di(hydroxy lower alkyl) amine oxide in which has about 10-20 carbon atoms in its first alkyl group, or an alkylmorpholine oxide containing 10-20 carbon atoms in its alkyl group.
3. A composition according to claim 1 or 2 wherein the chelating agent is selected from gluconic acid, tartaric acid, citric acid, oxalic acid, lactic acid, ethylenediaminetetraacetic acid, n-hydroxy ethylene diamine triacetic acid, nitrilotriacetic acid, diethylene triamine pentaacetic acid, and water soluble salts thereof.
4. A composition according to claim 3 wherein the chelating agent is a di-, tri- or tetra-sodium salt of ethylenediaminetetraacetic acid.
5. A composition according to any preceding claim wherein the water soluble amine containing organic compound is an alkanolamine containing no more than 20 carbon atoms.
6. A composition according to claim 5 wherein the alkanolamine contains no more than 6 carbon atoms.
7. A composition according to claim 6 wherein the alkanolamine is monoethanolamine.

8. A composition according to any of claims 1 to 4 wherein the water soluble amine containing organic compound further contains one or more ethoxy, propoxy or butoxy groups.
- 5
9. A composition according to claim 8 wherein the water soluble amine containing organic compound contains no more than 24 carbon atoms in its molecule.
- 10
10. A composition according to claim 9 wherein the water soluble amine containing organic compound contains no more than 12 carbon atoms in its molecule
11. A composition according to any preceding claim wherein the glycol ether solvent system comprises a first glycol ether having a solubility in water of not more than 20%wt., and a second glycol ether having a solubility of about 100%wt.
- 15
12. A composition according to any preceding claim wherein the composition has a pH of 12.5 or higher.
13. A composition according to claim 1 consisting ~~essentially~~ of:
- 20
- 0.5 - 0.8%wt. of the amine oxide based nonionic surfactant compound;  
0.2 - 0.6%wt. salt of ethylenediamine tetraacetic acid;  
0.1 - 0.5%wt. alkali metal hydroxide;  
1.5 - 4.0%wt. alkanolamine;  
5.0 - 7.0%wt. of a glycol ether solvent system comprising one glycol ether solvent having a
- 25
- solubility in water of not more than 20%wt., and a second glycol ether having a solubility of about 100%wt. in water, wherein the ratio of the former to the latter is from 0.5:1 to 1.5:1'  
0 - 0.7%wt. of the soil anti-redeposition agent; and  
0 - 1.0%wt. of one or more constituents selected from: preservatives, buffers, pH buffering agents, fragrances, fragrance carriers and adjuvants which increase their miscibility in the
- 30
- aqueous compositions, colorants, hydrotropes, antifoaming agents, anti-oxidants, anti-corrosion agents, and thickening agents.
14. A composition according to claim 1 consisting of:  
0.5 - 0.8%wt. of the amine oxide based nonionic surfactant compound;

- 0.1 - 1.5%wt. of the chelating agent, preferably selected from citrate, gluconate and glucoheptonate salts, particularly sodium salts thereof;
- 0.1 - 0.5%wt. alkali metal hydroxide;
- 1.5 - 4.0%wt. alkanolamine;
- 5 5.0 - 7.0%wt. of a glycol ether solvent system comprising one glycol ether solvent having a solubility in water of not more than 20%wt., and a second glycol ether having a solubility of about 100%wt. in water, wherein the ratio of the former to the latter is from 0.5:1 to 1.5:1;
- 0 - 0.7%wt. of the soil anti-redeposition agent;
- 10 0 - 1.0%wt. of one or more constituents selected from: preservatives, buffers, pH buffering agents, fragrances, fragrance carriers and adjuvants which increase their miscibility in the aqueous compositions, colorants, hydrotropes, antifoaming agents, anti-oxidants, anti-corrosion agents, and thickening agents.
- 15 15. A composition substantially as hereinbefore described with reference to any of Examples 1 to 4.
16. A method for cleaning a hard surface having baked-on greasy or oily stains which includes the step of: applying to the stain an effective amount of a composition according to claim 1.



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Patent  
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Application No: GB 9708788.6  
Claims searched: 1 to 16

Examiner: Michael Conlon  
Date of search: 21 July 1997

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C5D (DJX, DHX, DHZ)

Int Cl (Ed.6): C11D

Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	EP0621335 A2 (Eastman)	1
A	EP0095045 A1 (Karcher)	1
A	WO94/22996 A1 (Minnesota)	1
A	US5522942 (Reckitt & Colman)	1

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